

Optical and Structural Characteratization of Plasma Treated Zno Nano Particles Doped with PMMA Films

K. A. Vijayalakshmi^a and R. Deepa^b

^aAssistant Professor,
Sri Vasavi College Erode, INDIA.

^bResearch Scholar,
Plasma Physics Laboratory, Department of Physics, Sri Vasavi College Erode, INDIA.
email:Kumardeepa00@gmail.com

*Presented in First National Conference on Thin Film Science and Nano Technology
(FIRST-NCTFSANT-2013) September 2-3, 2013, Rajah Serfoji Govt. College, Thanjavur, T.N.(India).*

ABSTRACT

Zinc oxide nano particles were prepared by using solgel method. Nano particles of zno doped with PMMA (poly methyl methacrylate) polymer and the films were prepared by dipcoating method for different temperature. The PMMA/Zno film was plasma treated using DC glow discharge plasma. The treated and untreated films were characterized by uv-visible and XRD analysis. From the various results such as transmittance, bandgap energy and crystal nature of untreated films were compared with the plasma treated films.

Keywords: PMMA/Zno film, plasma exposure, Band gap, x-Ray diffraction.

INTRODUCTION

Nano composites are a special class of materials having unique properties and wide application potential in diverse areas. Novel properties of nano composites can be obtained from successful joined characteristics of parent constituents in a single material. These materials are different, as both materials like pure

polymers inorganic nanoparticles with some physical and chemical properties. Synthesis of inorganic particles in organic media is attractive because it produces particles with an organophilic surface originating from an organic medium or its degradation products. Zno, as one of the multifunctional inorganic nanoparticles has drawn increasing attention in recent years due to its many significant physical and chemical stability¹⁻³. Whereas

poly methyl methacrylate is a thermoplastic material with outstanding optical properties and favorable mechanical as well as processing properties⁴. By combining the nano ZnO and PMMA polymer, providing that homogeneous particle distribution in the polymer is achieved. For that reason the particle surface needs to be hydrophobically modified⁵⁻¹⁰. In recent years several methods have been developed to modify polymer surface¹¹. DC glow discharge plasma treatment has been successfully used as a dry process to alter the surface properties of polymers. The effect of plasma treatment depends on a variety of parameters such as the kind of plasma (DC, RF, or microwave) discharge power density, the pressure and the rate of gas or gas mixture, as well as the treatment time that significantly, reactive plasmas is used to add a polar function group (hydroxyl, carboxyl, ether, carbonyl, etc)¹². Which can dramatically increase the surface free energy of the nanooxide /polymer. In the present work ZnO nano /PMMA films were treated with DC glow discharge plasma with an aim of improving the optical properties. The plasma treated ZnO nano/PMMA film was characterized by XRD and UV-Visible studies. From various results such as transmittance, band gap and crystal nature of untreated films were compared with the plasma treated films.

EXPERIMENTAL SETUP AND METHODOLOGY

Synthesis of ZnO nano particles

ZnO nano particles are prepared by solgel method in the reaction of Zn^{2+} and OH^- . A solution containing zinc acetate dihydrate ($\text{Zn}(\text{ac})_2$) in 50ml of dimethyl

formamide (DMF) and another solution containing 0.5gm of NaOH in 50ml of dimethyl formamide were added with magnetic stirring at a temperature of 333K for 2 hours. Then, the precipitate was separated from the solution by centrifugation, washed several time with distilled water and then dried in air oven at 443K to obtain ZnO nano particles.

Preparation of ZnO nano/PMMA films

ZnO nano particles doped with PMMA (polymethyl methacrylate) polymer by magnetic stirring. A solution containing PMMA (1.25gm) in 100ml of DMF is added with synthesised ZnO nano powder. The solution was then heated at a constant temperature of 60°C with constant stirring. After stirring for 2hrs, the glass substrate is dipped in the solution for 30mins. The films were prepared and allowed to annealing at 60°C in an air oven. A well-dispersed film of ZnO nano inserted into PMMA was obtained.

Plasma Exposure

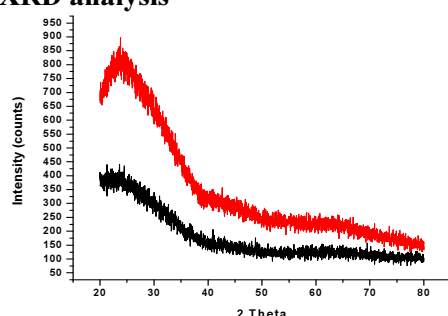
The coated ZnO nano PMMA films were exposed to DC glow discharge plasma of low –pressure was generated in a stainless steel chamber 50cm length and 30cm internal diameter. Vacuum of 10^{-3} mbar was maintained inside the chamber using a vacuum pump. Required vacuum was maintained of fine control gas needle valve piranigauge was used for pressure measurement. Circular shaped electrodes made of aluminium with a diameter of 6cm were fixed inside the chamber. The electrodes were separated by a distance of 3cm. High tension DC power supply 1.5Kv was used. The films were placed perpendicular to the discharge axis between

the parallel electrodes using a holder. After the plasma treatment the treated film was analyzed. The operating parameters influence the surface modification of the film. The operating parameters are listed in Table.

Discharge potential	400v
Pressure	0.3mbar
Exposure time	5mins
Electrode separation	3cm
Samples	Zno nano/PMMA film

RESULTS AND DISCUSSION

XRD analysis



XRD spectrum of Zno nano/PMMA film

The presence of the main peak at 25.3(2 theta value) confirmed the anatase

type crystal structure which was not influenced by plasma treatment. However Full width half maximum progressively increases with increase in the discharge potential which may be attributed to the increase in crystallinity of Zno. From these results we confirm that the plasma treatment although does not modify the anatase structure, it considerably improves the degree of crystallinity of the Zno film surface.

UV-Visible studies

Optical Transmittance were recorded on an Ultraviolet-Visible (UV-VIS) spectrometer over the range 0-2000nm. This covered the entire ultraviolet, visible and higher energy part of near infrared region. The transmittance range of the film indicates the suitability of optical application.

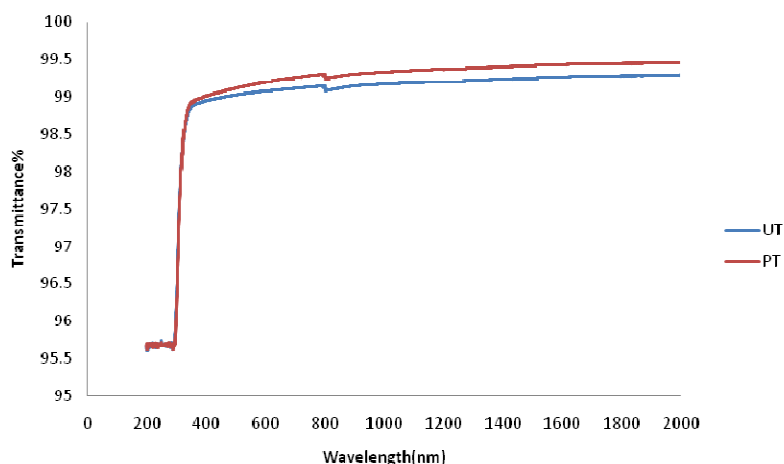


Figure:2 Transmittance spectra of Zno-nano/ PMMA films at room temperature for plasma treated and untreated film.

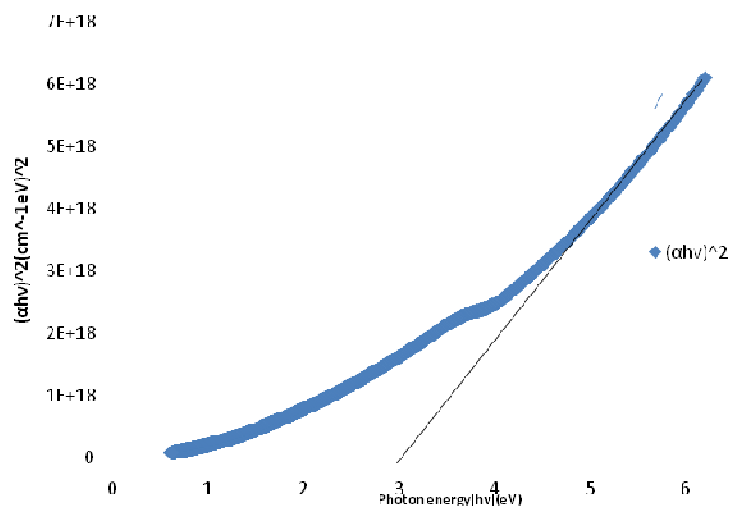


Figure:3 Band gap energy of ZnO nano /PMMA film

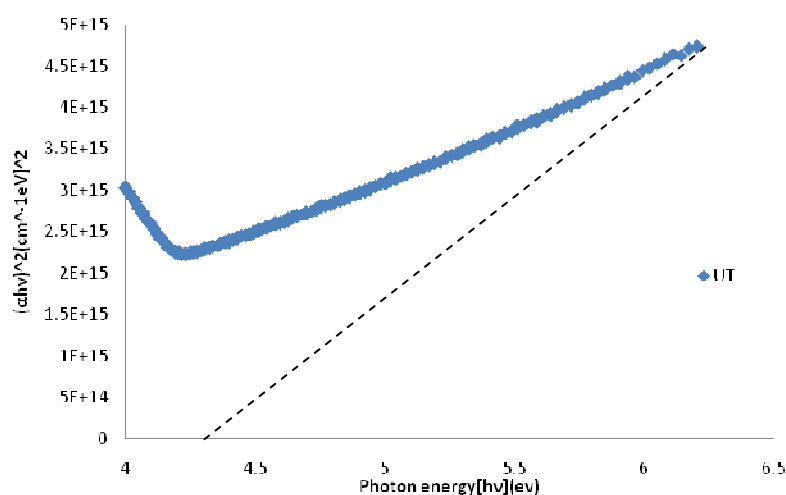


Figure:4 Band gap energy of ZnO nano/ PMMA film after plasma treatment

The absorption peak was observed around 280nm at room temperature for plasma treated and untreated films. Figure (2) shows the UV-Visible transmittance spectra of plasma treated and untreated films. ZnO nano particles not only absorb UV light but also scatter the visible light. This result shows the 99% transparency of

the ZnO nano/PMMA film and the larger transmittance window in the visible region enables very good optical applications.

Optical band gap

From the UV-Vis spectra, the optical (energy)band gap is determined by

translating the spectra into Tauc's plot¹³. The frequency-dependent absorption coefficient is given by

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g),$$

Where A is the parameter that depends on the interband transition probability, E_g the optical band gap, α the absorption coefficient, $h\nu$ the incident light energy and n is a number, characterizing the nature of transition process, i.e. n=2 indicates direct transition¹⁴.

Figure (3) and (4) reveals the band gap energy of the untreated and plasma treated film. From the study we observed that the band gap energy of the plasma treated film was (4.3eV) greater than the untreated film (3eV).

CONCLUSION

The results of XRD analysis of the ZnO nano/ PMMA film confirmed that the plasma treatment does not modify the crystallinity of film surface. From the UV-Visible analysis, found that the plasma treatment increase the band gap energy of the ZnO nano/PMMA film. This property indicates the transparency nature of the film. Finally the UV-Visible characteristic study reveals that the film was very good in optical applications.

REFERENCES

1. R.Wu, C.S. Xie, Formation of tetrapod ZnO nanowhiskers and its optical properties, *Mater. Res. Bull* (2004).
2. M. Kitano, M. Shiojiri, Bernard convention ZnO/resins lacquer coating a new approach to electrostatic dissipative coating, *Powder Technol.* (1997).
3. Yang Y, Chen HL, Zhao B, Bao XM. Size control of ZnO nanoparticles via thermal decomposition of zinc acetate coated on organic additives. *J. Cryst. Growth* (2004).
4. Demir M.M., Memesa M., Castignolles P., Wegner G. PMMA/zinc oxide nano composite prepared by in-situ bulk polymerization. *Macromolecular Rapid communications*, 27, 763-770 (2006). DOI:10.1002/marc.200500870
5. Munoz-Espi R., Jeschke G., Lieberwirth I., Gomez C.M., Wegner G. ZnO-latex hybrids obtained by polymer- controlled crystallization: A Spectroscopic investigation. *Journal of Physical Chemistry B*, 111, 697-707 (2007). DOI:10.1021/jp066380d
6. Golovko D.S., Munoz – Espi R., Wegner G. Interaction between poly (styrene-acrylic acid) latex nano particles and zinc oxide surfaces. *Langmuir*, 23, 3566-3569 (2007). DOI:10.1021/la 0632880
7. Kickelbick G. Concepts for the incorporation of inorganic building blocks into organic polymers on a nano scale. *Progress in Polymer Science*, 28, 83-114 (2003).
8. Khrenov V., Klapper M., Mullen K. Surface functionalized ZnO particles designed for the use in transparent nano composites. *Macromolecular chemistry and Physics*, 206, 95-101 (2005). DOI:10.1002/macp.200400213
9. Khrenov V., Schwager F., Klapper M. Koch M., Mullen K. Compatibilization of inorganic particles for polymeric nano composites. Optimization of the size and the compatibility of ZnO particles polymer Bulletin, 58, 799-807 (2007).

- DOI: 10.1007/S00289-006-0721
10. Hong R. Y., Quian J. Z., Cao J.X. Synthesis and characterization of PMMA grafted ZnO nano particles powder Technology, 163, 160-168 (2008).
DOI:10.1016/j.powtec.2006.01.015
 11. Eliston, L.Martinu, M. Wertheimer, *J. Adhesion Science, Technology*, 7, 1091, (1992).
 12. S. Kitova, V. Strijkova and G. Danev, 36th EPS Conference on plasma physics, Sofia, *EVA* Vol. 33 EP-1.038, June 29-July 3, (2009).
 13. Bhuvana, K. Periyasamy, Robinson S. Jebas, N. Gopalakrishanan, and T. Balasubramanian, Development of NLO tunable band gap organic devices for optoelectronic applications.
 14. I. Waterbe, T.Okumura, *Japanese Journal of Applied physics* 25, 1851-1854 (1986).